

## Coal Ash Analysis with an Argon Plasma Emission Excitation Source

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(Received 27 April 1972; revision received 29 June 1972)

INDEX HEADINGS: Atomic emission spectroscopy; Applications; Analysis of coal ash.

Knowledge of the composition of coal ash and related materials has become important today in the investigation of air and water pollution, coal miners' pneumoconiosis, and strip mine reclamation as well as in the traditional investigation of clinkering and slagging problems in industrial use. Simplified procedures are needed to analyze these materials. In 1962, Gibson and Ode<sup>1</sup> published a rapid method for analyzing coal ash based on colorimetric, flame photometric, and chelatometric titration techniques. This procedure, although faster and more direct than classical wet chemical procedures, requires two dissolutions per sample plus numerous reagents and dilutions. A more desirable route to the analysis of coal ash would involve the preparation of a single solution that could be analyzed directly.

The application of a lithium metaborate fusion has enabled coal ash samples to be completely analyzed with one dissolution. Atomic emission analysis<sup>2</sup> has allowed direct quantitative analysis of the constituents in coal ash from the single dissolved sample. A qualitative analysis of the sample for trace constituents can also be rapidly obtained from a single photograph of the spectrum resulting from excitation of either the solid or dissolved coal ash. This paper describes the analysis of the constituents in two coal ash samples and National Bureau of Standards (NBS) standard 1A, Argillaceous limestone, by atomic emission and

compares the results with values obtained by the Gibson and Ode method.

Two instruments were available for atomic emission: (1) a SpectraSpan model 101 echelle spectrometer<sup>2</sup> for photographic measurements and sequential photoelectric determinations of elemental constituents and (2) a SpectraSpan model 210 multielement echelle spectrometer with digital readout for simultaneous determinations of elemental constituents. (Equipment is named in this report for identification only and does not necessarily imply endorsement by the Bureau of Mines.) The model 101 was equipped with a Bausch and Lomb V.O.M.-5 recorder. A high temperature argon plasma SpectraJet<sup>3</sup> was utilized as the excitation source for dissolved samples. Solid samples were excited by a dc arc, utilizing graphite electrodes. Power requirements were 7 A and 32 V. The total argon gas flow was 10 SCFH (approximately 5 liters/min), jet cathode flow was 0.5 SCFH (approximately 0.2 liter/min), and jet anode flow was 2 SCFH (approximately 1 liter/min) with a sample rate of 1 ml/min. A 200- $\mu$  entrance slit was used. Integration time ranged between 15 and 30 sec. Spectra of the excited samples were photographed on 4  $\times$  5-in., type 55 positive/negative Polaroid film, ASA 50.

A Beckman model DU quartz spectrophotometer was used for colorimetric determinations, and a Beckman model DU flame spectrophotometer was used for flame photometric determinations.

North Dakota lignite and West Virginia bituminous coal were analyzed. Ash samples were prepared by heating the coals at 800°C until the weight was constant or loss was less than 0.5%/h. Standard solutions were prepared, following the procedure below, from coal ashes that had been previously analyzed by the Gibson and Ode method. Synthetic standards were similarly prepared from mixed reagent grade oxides of the elements.

Sample constituents for the atomic emission analysis were solubilized by a lithium metaborate fusion.<sup>4-6</sup> A 0.2000-g sample of -100 mesh coal ash was mixed with 2.0 g of lithium metaborate in a platinum crucible and heated at 950°C in a muffle furnace for 25 min. The melt was swirled onto the sides of the crucible, then quenched in a Teflon beaker containing 100 ml of 4% nitric acid. The beaker was then placed in an ultrasonic vibrator until solution was complete. The solution was diluted to 200 ml and stored in a plastic bottle. It was not necessary to add protective or releasing agents to prevent interelemental interferences

TABLE I. Results of quantitative analysis, percent oxide.<sup>a</sup>

Oxide	Wave length used on Spectra-Span (Å)	W. Va. bituminous coal			North Dakota lignite			NBS 1A		
		Gibson and Ode method	Spectra-Span 101	Spectra-Span 210	Gibson and Ode method	Spectra-Span 101	Spectra-Span 210	Certified analysis	Gibson and Ode method	Spectra-Span 101
SiO <sub>2</sub>	2881.58	40.6	40.6	40.5(s) 40.4(s)	20.8	21.3	21.5(s) 21.4(s)	14.1	14.1	14.4
Al <sub>2</sub> O <sub>3</sub>	3944.03	23.9	24.3	24.3(s) 24.1(s)	13.7	13.0	12.9(s) 13.1(s)	4.16	4.26	4.10
Fe <sub>2</sub> O <sub>3</sub>	3719.93	22.3	22.5	22.6(s) 22.6(s)	8.59	8.72	8.67(s) 8.77(s)	1.63	1.62	1.55
TiO <sub>2</sub>	3349.03	0.50	0.54 0.57(s) 0.56(s)		0.26	0.26 0.23(s) 0.26(s)		0.16	0.15	0.15
P <sub>2</sub> O <sub>5</sub>	2535.65	0.42	0.38(s) 0.42(s) 0.43(s)		0.09	0.12(s) 0.14(s) 0.14(s)				
CaO	3933.67	4.62	4.59	4.61(s) 4.65(s)	20.4	20.6	20.5(s) 20.6(s)	41.3	41.3	41.6
MgO	2802.70	0.81	0.83	0.81(s) 0.84(s)	5.17	5.31	5.25(s) 5.30(s)	2.19	2.27	2.30
Na <sub>2</sub> O	5889.95	0.73	0.69	0.68(s) 0.70(s)	9.7	10.6	10.3(s) 10.2(s)	0.39	0.31	0.37
K <sub>2</sub> O	7664.91	1.37	1.41(s) 1.38(s) 1.39(s)	1.40(s) 1.41(s)	0.68	0.67(s) 0.67(s) 0.70(s)	0.70(s) 0.70(s)	0.71	0.83	

<sup>a</sup> (s), analyzed at Spectrametrics, Inc., Burlington, Massachusetts 01803.

between Ca, P, Al, and Si because of the high temperature of the argon plasma.<sup>3</sup>

Si, Al, Fe, Ti, P, Ca, Mg, Na, and K were measured in each dissolved sample sequentially on the model 101 and simultaneously on the model 210. Results are shown in Table I. The total elapsed time for the analysis of a single sample was 4 h on the model 101 and 1 h on the model 210.

The Gibson and Ode method required the preparation of two solutions. Silicon and aluminum were determined on a solution prepared from a sodium hydroxide fusion of the coal ash. The remaining constituents were determined on a solution prepared by digesting the ash in sulfuric, hydrofluoric, and nitric acid.

Si, Al, Fe, Ti, and P were determined colorimetrically; Na and K were determined by flame photometry; and Ca and Mg were determined by titration with disodium ethylenediaminetetraacetate. Results are shown in Table I. The total elapsed time for the analysis of a single sample was 30 h.

Table I shows the results as percent oxide for the two coal ash samples and NBS standard 1A. Those results designated with (s) were done at Spectrametrics, while those unmarked were made at the Morgantown Energy Research Center. Each result reported on each element analyzed was obtained from a separate sample dissolution. The results of the two methods, as well as of the same method utilized in the two laboratories, compared favorably except for the unaccountably high sodium and phosphorus values in the North Dakota lignite.

Each coal ash sample, both solid and dissolved, was

subjected to spectrographic qualitative analysis, and trace constituents were identified. The identification of a trace element was confirmed by the presence of three characteristic spectral lines, with the exception of boron, which has only two major lines.

Spectrograms of the solid bituminous ash indicated the presence of Ag, B, Ba, Bi, Co, Cu, Cr, Mn, Mo, Ni, Pb, Sn, V, Zn, and Li in addition to the major elements. The dissolved bituminous ash contained the same elements plus platinum from the slight attack of the flux on the crucible. The spectrograms of the solid and dissolved lignite showed the presence of the same elements as above except that Mn was absent.

Lithium metaborate fusion of the coal ash and NBS standard 1A, followed by atomic emission analysis on the SpectraSpan 101 and 210, is faster than the Gibson and Ode method without any apparent loss of accuracy. This procedure can be extended to the analysis of various residues, slags, fly ashes, and other materials that are related to the coal industry. In addition, the spectrogram provides a rapid method of qualitative analysis of the sample, as well as permanent documentation.

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